

^{139}La NMR investigation in underdoped $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ S.-H. Baek,^{1,*} A. Erb,² B. Büchner,¹ and H.-J. Grafe¹¹*IFW-Dresden, Institute for Solid State Research, PF 270116, 01171 Dresden, Germany*²*Walther-Meißner-Institut, Bayerische Akademie der Wissenschaften,
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We report ^{139}La and ^{63}Cu nuclear magnetic and quadrupole resonance (NMR/NQR) studies in an underdoped $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ single crystal, focusing on the ^{139}La NMR in the normal state. We demonstrate that the local structural distortions in the low-temperature orthorhombic structure cause the tilting of the direction of the electric field gradient (EFG) at the nuclei from the c axis, resulting in two NMR central transition spectra at both the ^{139}La and ^{63}Cu nuclei in an external field. Taking into account the tilt angle of the EFG, the temperature dependence of the ^{139}La spectra allowed us to determine the ^{139}La Knight shift and the structural order parameter. The angle and temperature dependence of the ^{139}La spectrum is in perfect agreement with the macroscopic average structure and proves a displacive transition. The ^{139}La nuclear spin-lattice relaxation rates, T_1^{-1} , suggest that $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ undergoes a gradual change to a temperature-independent paramagnetic regime in the high temperature region. Both the spectra and T_1^{-1} of the ^{139}La as a function of temperature reveal a sharp anomaly around $T_S = 387(1)$ K, implying a first-order-like structural transition, and a dramatic change below ~ 70 K arising from collective glassy spin freezing.

I. INTRODUCTION

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) is a single-layered cuprate where the CuO_2 planes are separated by a $\text{La}_{2-x}\text{Sr}_x\text{O}_2$ block layer. A mismatch between the CuO_2 planes and the interlayer causes a structural transition from a high temperature tetragonal (HTT) to a low-temperature orthorhombic (LTO) phase,¹ where the CuO_6 octahedra are tilted from the c axis resulting in a buckling pattern of the CuO_2 plane. Further partial substitution of a rare earth element (Eu or Nd) at the La site, or replacement of Sr by Ba induces another structural transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ from the LTO to a low-temperature tetragonal (LTT) phase. In the LTT structure, the local tilt of the CuO_6 octahedra persists but its direction is rotated by 45° and alternates by 90° in neighboring planes yielding the macroscopic tetragonal symmetry. Such a local structural distortion as a function of doping has a large influence on the magnetic and superconducting phases.^{2–6} In particular, the LTT phase seems to be a prerequisite for static stripe order which may compete with superconductivity in cuprates.^{7–9}

In view of the intimate coupling of the respective structure to superconductivity, a detailed understanding of the *local* structure and its doping- and temperature-dependence is crucial to understand the high- T_c mechanism. Yet, there have been unsettled issues regarding the local structure such as whether the macroscopic average structure fully corresponds to the local one involving a displacive structural transition,^{10–12} or to a superposition of coherent local LTT variants involving an order-disorder transition.^{13–16}

While nuclear magnetic resonance (NMR) as a local probe is suitable to investigate the local structure, it is also extremely sensitive to inhomogeneities in the sample which often complicate the NMR spectra, leading to an erroneous analysis of the results. For example, the mag-

netic phase separation scenario¹⁷ in LSCO with $x = 0.06$ based on the splitting of the ^{139}La NMR spectrum turned out to be a misinterpretation,¹⁸ although its true origin has not been thoroughly understood.

In this paper, the local structure in a high quality $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ single crystal is investigated via ^{139}La NMR. The La site is most strongly affected by the local distortions associated with the structural phase transition,^{14,19} making the ^{139}La a suitable local probe for the local structure. Indeed, our ^{139}La NMR results show that the local tilting pattern of the CuO_6 octahedra in the LTO structure is accompanied by a tilting of the EFG at the nuclei, resulting in the splitting of the otherwise single resonance line. We confirmed that the ^{63}Cu spectrum splits into two in the LTO structure as well, but with a much smaller tilt angle than the value for the ^{139}La . A strong temperature dependence was found in the splitting of the ^{139}La spectrum, which measures the tilt angle of the CuO_6 octahedra which disappears abruptly above T_S . Our NMR data thus provide an evidence that the macroscopic average structure parameters are sufficient to account for the local lattice distortions and their temperature dependence. In addition, the ^{139}La spin-lattice relaxation rates measured in a wide temperature range are discussed.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The crystal of $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ ($T_c = 14$ K) has been grown from 4N materials of La_2O_3 , SrCO_3 , and CuO using the TSFZ (Traveling Solvent Floating Zone) technique. Using this technique, which is described in detail elsewhere,²⁰ large crystals of several centimeters length can be grown under accurately controllable stable conditions (flux composition, temperature and oxygen par-

tial pressure), which in terms are the prerequisite for homogeneous crystals. The sample for the NMR measurements was cut out of a single crystalline rod after the growth procedure along the crystallographic a , b , and c -axis using the Laue x-ray method. The outer dimensions measured 1.7 mm, 2.5 mm, and 0.8 mm in a , b , and c -direction.

^{139}La ($I = 7/2$) and ^{63}Cu ($I = 3/2$) NMR experiments were performed on the single crystal of $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ in the range of temperature 4.2–420 K. The sample was mounted on a goniometer which allows an accurate alignment of the sample along the external field. In order to check the quadrupole frequency ν_Q , the ^{139}La NQR spectrum at the $3\nu_Q$ ($\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$) transition (~ 18.9 MHz) and the ^{63}Cu NQR spectrum at the ν_Q ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) transition (~ 34 MHz) were measured. The NMR/NQR spectra were acquired by spin-echo signals as the frequency was swept through the resonance line using Hahn echo sequence ($\pi/2 - \tau - \pi$) with $\pi/2 \sim 2 \mu\text{s}$.

The nuclear spin-lattice relaxation rates T_1^{-1} were measured at the central transition of the ^{139}La by the saturation recovery method and the relaxation of the nuclear magnetization after a saturating pulse was fitted to the following equation:

$$1 - \frac{M(t)}{M(\infty)} = a \left(\frac{1}{84} e^{-t/T_1} + \frac{3}{44} e^{-6t/T_1} + \frac{75}{364} e^{-15t/T_1} + \frac{1225}{1716} e^{-28t/T_1} \right), \quad (1)$$

where M is the nuclear magnetization and a a fitting parameter that is ideally one.

III. RESULTS AND DISCUSSION

A. ^{139}La NMR spectra

Figure 1 shows the central transition NMR spectrum of the ^{139}La at 300 K and 10.7 T as a function of the angle θ between the crystallographic c axis and the external field H . The ^{139}La spectrum consists of two resonance lines which both exhibit the same angle dependence with respect to H : the peaks are centered at $\theta_m^\pm = \pm 8^\circ$, respectively, where the maximum resonance frequencies are observed. The two angle-dependent sets of the ^{139}La spectrum which are symmetric around the c axis imply the existence of two different sites with the same occupation probability.

Such a strong angle dependence of the central transition is expected from second order quadrupole interaction of the nuclear quadrupole moment Q that is non-zero for the nuclear spin $I > \frac{1}{2}$, with the EFG. For the central transition ($-\frac{1}{2} \leftrightarrow \frac{1}{2}$), while the first order quadrupole shift is zero, the second order quadrupole shift is given

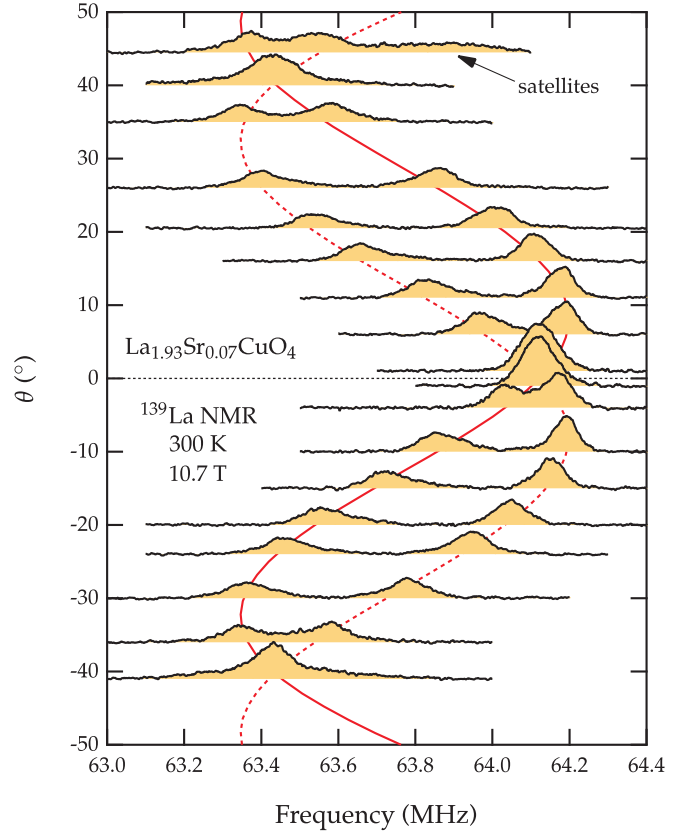


FIG. 1: Angle dependence of ^{139}La NMR spectra measured at room temperature and 10.7 T. Solid (dotted) lines are theoretical calculations assuming 8° (-8°) tilting of the principal axis of the EFG from the c axis, using $\mathcal{K} = -0.09\%$ and $\nu_Q = 6.3$ MHz which were determined experimentally from this study. The anisotropy parameter $\eta = 0.19(2)$ was obtained from the calculations.

by²¹

$$\Delta\nu^{2\text{nd}} = \frac{\nu_Q^2}{32\gamma_n H} (1 - \cos^2 \theta) \left[2I(I+1) - \frac{3}{2} - \left(18I(I+1) - \frac{27}{2} \right) \cos^2 \theta \right], \quad (2)$$

where γ_n is the nuclear gyromagnetic ratio and ν_Q is the quadrupole frequency given by $3e^2qQ/2I(2I-1)\hbar$ where eq is the EFG. Here, without the loss of generality, we ignored an anisotropy parameter η which is non-zero in sites of lower than axial symmetry. From Eq. (2), one can see that when $\theta = 0$, $\Delta\nu = 0$ so that the resonance frequency becomes one of the maxima and directly yields the Knight shift since a quadrupole correction is not needed.

It may be possible that the ^{139}La is differentiated due to the presence of two EFG strengths which would cause the different quadrupole shift at the nuclei. To check the possibility, we measured the ^{139}La NQR spectrum in zero field at the $3\nu_Q$ transition. Since a well-defined

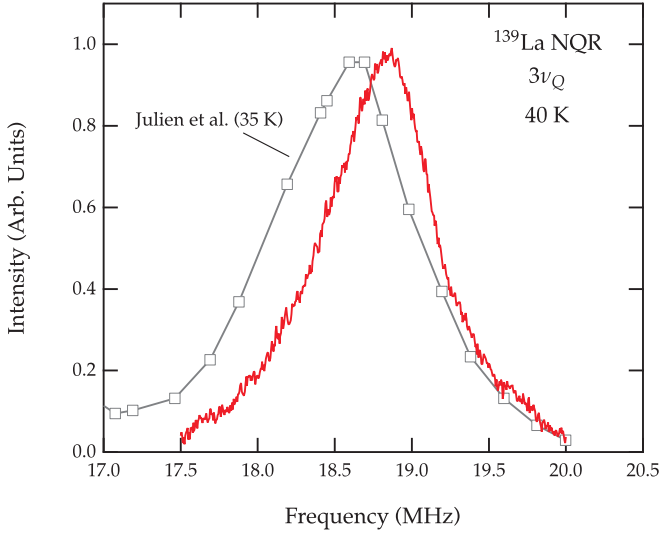


FIG. 2: ^{139}La NQR spectrum measured at the $3\nu_Q$ transition at 40 K giving rise to $\nu_Q = 6.3$ MHz. The NQR spectrum from Julien et al.¹⁸ measured in the sample of $x = 0.1$ is compared. The narrower linewidth of our NQR spectrum indicates less chemical inhomogeneity in the single crystal.

single NQR line as shown in Fig. 2 indicates the unique value of the EFG in the system, the two ^{139}La peaks are attributed to the local tilting of the direction of the EFG at the ^{139}La with respect to the c axis,²² where θ_m corresponds to the angle at which the direction of the EFG is parallel to \mathbf{H} .

In order to confirm this quantitatively, we performed exact diagonalization calculations of the nuclear Hamiltonian which can be written as,

$$\mathcal{H} = -\gamma_n \hbar [1 + \mathcal{K}(\theta)] \mathbf{I} \cdot \mathbf{H} + \frac{\nu_Q}{6} [3I_z^2 - I^2 + \eta (I_x^2 - I_y^2)], \quad (3)$$

where \mathcal{K} is the Knight shift which is usually angle dependent and I is the nuclear spin operator.

In the calculations, we used $\nu_Q = 6.3$ MHz from the $3\nu_Q$ transition (Fig. 2) and $\mathcal{K} = -0.09\%$ (Fig. 6). Here we neglect a possible angle dependence of \mathcal{K} . Thus, η is the only unknown parameter in the Hamiltonian. By adjusting η , we accurately reproduced the resonance frequencies of the spectra as a function of θ , drawn as solid (dotted) lines in Fig. 1. From these calculations, the anisotropy parameter $\eta = 0.19(2)$ was deduced. Since η can absorb the effect of the angle variation of \mathcal{K} , the actual value may slightly differ from the one deduced here. The excellent agreement of the theory with the experimental data indicates a staggered pattern of the tilting of the EFG at the ^{139}La around the c axis, due to the corresponding local structural distortions.

As a matter of fact, this is well supported by the LTO structure in Fig. 3, which was drawn using structure parameters for $x = 0.075$ at 10 K given in Ref. 19. Clearly,

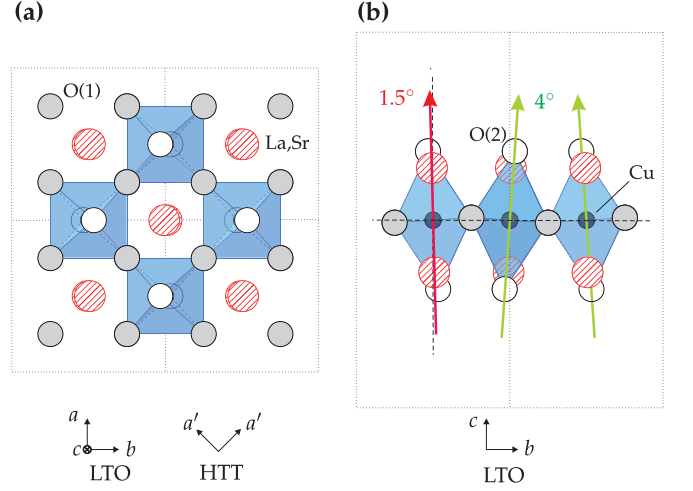


FIG. 3: Structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the LTO phase at 10 K for $x = 0.075$, using the structure parameters reported in Ref. 19, viewed along $[001]$ (a) and along $[100]$ (b). The unit cell is depicted as the dotted line. The CuO_6 octahedra is tilted along the $[010]_{\text{LTO}}$ (or $[110]_{\text{HTT}}$) direction by 4° . In addition, $\text{La}(\text{Sr})$ - $\text{La}(\text{Sr})$ along the c axis is tilted by 1.5° in opposite direction of the distortion of the CuO_6 octahedra, being consistent with a much larger tilted angle of the EFG at the ^{139}La . Note that the tilt direction of both the CuO_6 octahedra and the La-La is maintained along $[010]_{\text{LTO}}$, whereas, along the diagonal direction i.e., $[110]_{\text{LTO}}$, it is rotated alternately by 180° , causing the so called *buckling* of the CuO_2 plane.

the main axis of the CuO_6 octahedra is tilted by 4° along the $[010]$ direction (or $[110]$ in the HTT setting). In addition, the position of $\text{La}(\text{Sr})$ with respect to the c axis is slightly shifted in opposite direction of the distortion of the CuO_6 octahedra, which may cause a larger tilting of the EFG at the ^{139}La than at the ^{63}Cu . Furthermore, the fact that the tilt direction of the octahedra is reversed alternately along the $[110]_{\text{LTO}}$, which induces the buckling of the CuO_2 planes,^{2,7} accounts for the two ^{139}La peaks whose intensities and positions as a function of θ are symmetric around the c axis.

If the two ^{139}La NMR lines are the result of the distorted CuO_6 octahedra in the LTO phase, one should expect that there are two Cu sites which are distinguishable in field as well. However, the presence of the two central transitions of the ^{63}Cu has not been reported so far. It may be possible that the tilt angle of the EFG at the ^{63}Cu is too small to be detected, especially with the relatively larger linewidth of the ^{63}Cu NMR spectrum than that of the ^{139}La . In order to check whether there exist two ^{63}Cu NMR lines in the LTO phase, the ^{63}Cu spectrum has been carefully examined by varying θ at 300 K. Indeed, as shown in Fig. 4, the angle dependence of the ^{63}Cu spectrum unravels two central transitions which are centered at $\theta_m^\pm = \pm 2^\circ$ respectively, being symmetric around the c axis. The solid (dotted) lines are from theoretical calculations with Eq. (3) using the

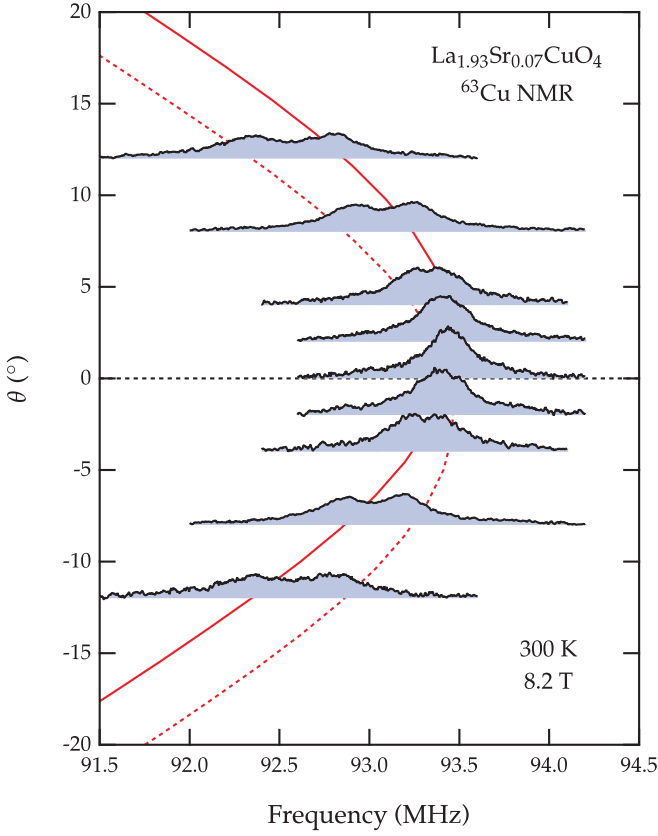


FIG. 4: Angle dependence of the ^{63}Cu NMR spectra measured at 300 K and 8.2 T. The solid (dotted) lines are theoretical calculations assuming 2° (-2°) tilting of the direction of the EFG at the ^{63}Cu from the c axis, with parameters $\nu_Q = 34$ MHz, $K = 1.18\%$, and $\eta = 0$.

values of parameters, $\nu_Q = 34$ MHz and $K_c = 1.18\%$. Unlike the case of the ^{139}La , a non-zero η is not needed to fit the data. The negligible η and the much smaller θ_m than that of the ^{139}La are also consistent with the LTO structure depicted in Fig. 3, where the La itself is displaced. Therefore, we conclude that the two peaks at both the ^{139}La and the ^{63}Cu are a natural consequence of the HTT-LTO structural transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

We are aware that the qualitatively similar argument was given by Julien *et al.*¹⁸ where they observed four ^{139}La peaks which were attributed to the tilting of the direction of the EFG about the c axis. However, the four peaks with various signal intensities and linewidths are difficult to understand in detail and are not in accordance with only two different La sites as expected for the LTO structure. We conjecture that the sample used by Julien *et al.* consisted of two or more domains which have slightly different orientations.

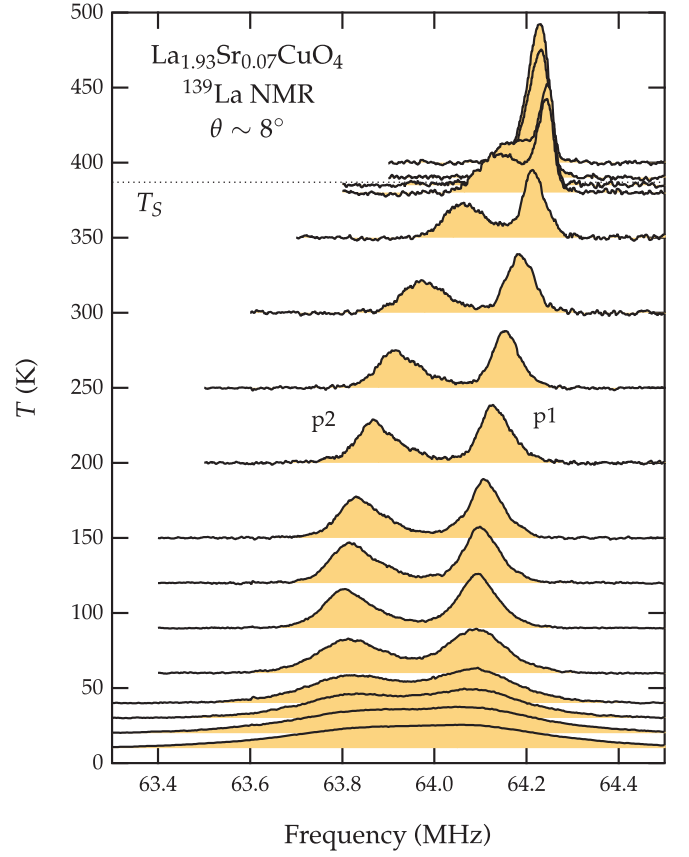


FIG. 5: Temperature-dependence of the ^{139}La NMR spectra in an external field tilted by $\theta \sim 8^\circ$ from the crystallographic c axis. In this case, p1 corresponds to the line in which the EFG at the ^{139}La is aligned along H , giving rise to the Knight shift for $H \parallel c$ since there is no quadrupole shift. At 387 K, the two peaks collapse to a single peak, indicating the LTO-HTT structural transition. At low temperatures, ^{139}La spectrum is significantly broadened, implying the slowing down of the spin fluctuations due to the spin-density wave (SDW) order. Each spectrum was scaled with temperature to remove the Boltzmann contribution to the intensity.

B. ^{139}La Knight shift and structural order parameter

Next we discuss the temperature dependence of the ^{139}La spectra. In order to extract the Knight shift for $I > 1/2$ in non-axial symmetry, the second order quadrupole effect which shifts the central transition, as given by Eq. (2), should be taken into careful consideration, particularly for a very small Knight shift which is the case for the ^{139}La NMR in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Taking advantage of the fact that the second order quadrupole shift vanishes when H is applied along the direction of the EFG, we deliberately rotated the sample with respect to the c axis by 8° . Then, the second order quadrupole shift for the peak p1 is zero and the intrinsic Knight shift as a function of temperature could be extracted.

With increasing temperature from 300 K, the sepa-

ration between the two peaks becomes smaller and the spectra collapse abruptly into single spectrum at $T_S = 387(1)$ K, the structural transition temperature T_S from the HTT to the LTO phase.^{1,23} This is another direct evidence that the two ^{139}La central peaks arise from the tilted CuO_6 octahedra associated with the LTO structure. The T -dependence of the resonance frequencies of the two lines is shown in Fig. 6(a). The single line above T_S is split into two at T_S , in which one line (p1) shifts up and the other (p2) shifts down in frequency from the single line above T_S . The line p1 gives rise to the Knight shift for $H \parallel c$, \mathcal{K}_c , which is drawn in Fig. 6(b). Note that the Knight shift data above T_S is obtained after rotating back the sample along the c axis, since the EFG should be directed along the crystallographic c axis in the HTT structure due to the axial symmetry with respect to the c axis.

Additional valuable information was obtained from Fig. 6(a). Just below T_S , the separation between p1 and p2 rapidly increases but approaches a constant value at low temperatures, that is, the separation between the two lines $\Delta\nu$ as a function of temperature behaves as the structural order parameter as shown in Fig. 6(b). At T_S , the transition is clearly discontinuous, indicating a first order nature of the transition, in contrast to second-order character reported in the diffraction measurement.² On the other hand, except for the discontinuous change at the transition, the temperature dependence of $\Delta\nu$ shows the behavior expected in a second order transition.

The narrow single resonance line in the HTT phase indicates that within the resolution of the NMR experiment the local tilting of the CuO_6 octahedra vanishes immediately above T_S rendering the local tetragonal symmetry, in contrast to the experimental reports that the LTO-type local tilt remains even in the HTT phase.^{14,24} Furthermore, the abrupt splitting of the spectrum at T_S confirms a displacive transition, not an order-disorder one.

Since $\Delta\nu$ is a measure of the tilt angle of the EFG at the nuclei, its rapid suppression with increasing temperature from 300 K toward T_S may cause a finite second order quadrupole shift affecting the ^{139}La Knight shift which was obtained with the tilt angle 8° determined at 300 K. Then, the actual Knight shift data just below T_S may be slightly enhanced, in such a way that data are smoothly connected to those in the HTT phase. Likewise, $\Delta\nu$ itself should be affected with a small error.

C. ^{139}La spin-lattice relaxation rate

Figure 7 shows the spin lattice relaxation rate T_1^{-1} of the ^{139}La as a function of temperature in the range 4.2–420 K. With increasing temperature from room temperature, T_1^{-1} is rapidly enhanced. We found a discontinuous jump at $T_S = 387$ K which is followed immediately by a steep drop above T_S . The sharp anomaly of T_1^{-1} around T_S is consistent with the drastic change of the ^{139}La spectrum at T_S (Fig. 5) and supports a first order

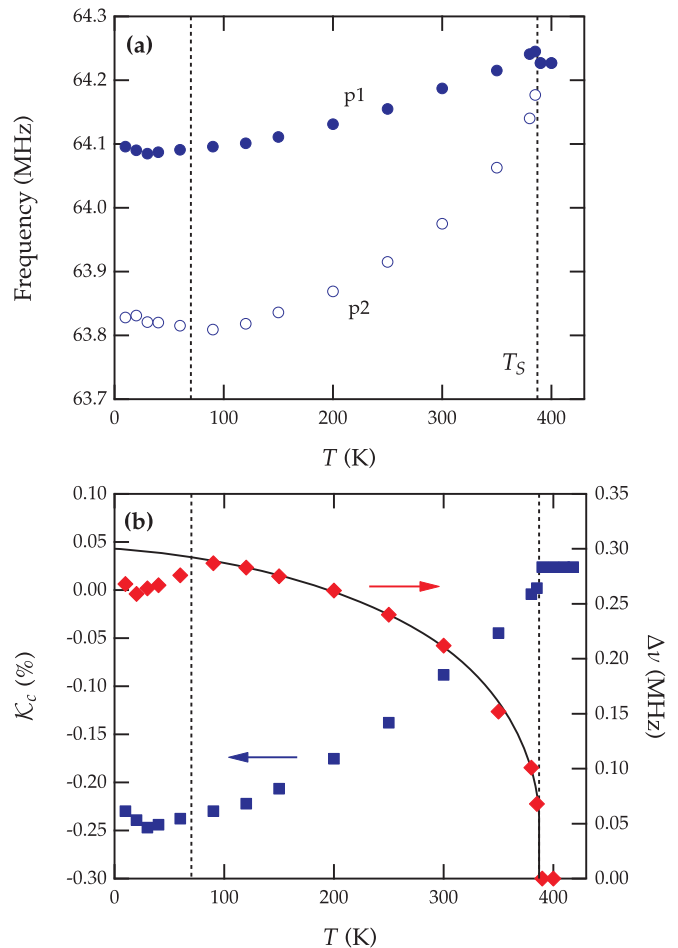


FIG. 6: (a) Temperature-dependence of resonance frequencies of two NMR peaks in Fig. 5. (b) Knight shift of the ^{139}La is extracted from the p1 line. The separation of the two peaks $\Delta\nu(T)$ behaves as a structural order parameter. $\Delta\nu$ reveals first order-like discontinuous transition at $T_S = 387$ K, while it exhibits the second order-like temperature dependence except the region of the transition. Solid line is a guide to eyes. Below 70 K, data deviate due to the onset of the magnetic broadening associated with the incommensurate SDW order.

structural transition. Upon further increasing the temperature, T_1^{-1} continues to increase up to 420 K which is a limitation of our equipment.

Interestingly, the temperature dependence of $^{139}\text{La} T_1^{-1}$ resembles that observed in $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$,^{5,25} where $^{139}\text{La} T_1^{-1}$ rapidly drops below the LTT-LTO structural transition. The HTT-LTO transition, however, is clearly manifested through an anomaly in the narrow range of temperature which is simply added on top of the rapid drop of T_1^{-1} . Note that T_1^{-1} already started to decrease at a much higher temperature than T_S .

Rather, we conjecture that the rapid upturn of T_1^{-1} is associated with a gradual change from a system with a local moment character to a more itinerant system, as argued by Imai *et al.*²⁶ They report that ^{63}Cu forms a broad maximum near 200 K in sim-

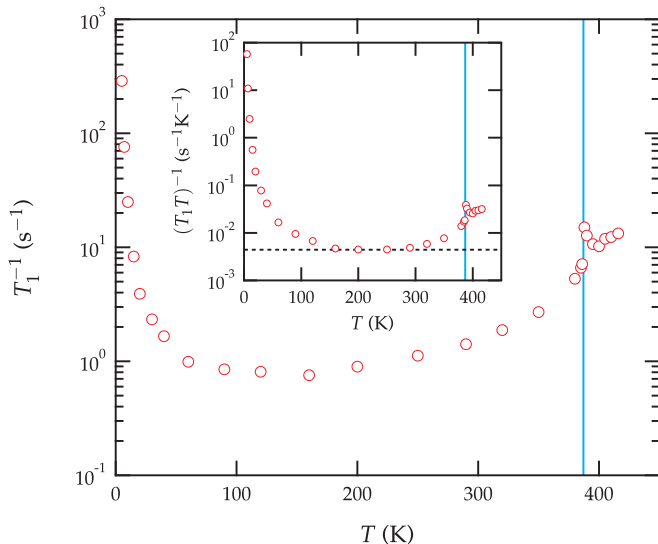


FIG. 7: ^{139}La T_1^{-1} as a function of temperature. A very sharp anomaly at $T_S = 387$ K was detected with the transition width less than 10 K. Below 70 K, the critical slowing down due to the SDW order causes extremely steep upturn of T_1^{-1} . Inset shows $(T_1 T)^{-1}$ of the ^{139}La versus temperature. Note that $(T_1 T)^{-1}$ increases more than four decades as the temperature increases from ~ 100 K down to 4.2 K.

ilarly Sr-doped samples, approaching a temperature independent value $^{63}\text{La} T_{1\infty}^{-1} \sim 2500 \text{ s}^{-1}$ at sufficiently high temperatures.^{26,27} If the temperature and doping independent $^{63}\text{La} T_{1\infty}^{-1}$ at $T \sim J_{\text{ex}}/2$, where J_{ex} is the exchange coupling constant, imply the exchange narrowed paramagnetic limit, one may expect that $^{139}\text{La} T_{1\infty}^{-1}$ should be dominated by J_{ex} and the hyperfine coupling A_{hf} according to the relation,^{28,29}

$$\frac{1}{T_{1\infty}} \propto \frac{A_{\text{hf}}^2 \sqrt{S(S+1)}}{J_{\text{ex}}}, \quad (4)$$

where we neglect an anisotropy of A_{hf} for simplicity. A very rough estimation from the Knight shift values, which are proportional to A_{hf} , obtained at room temperature gives $^{139}\text{La} T_{1\infty}^{-1} = ^{63}\text{La} T_{1\infty}^{-1} (^{139}\text{K}/^{63}\text{K})^2 \sim 10 \text{ s}^{-1}$ which is surprisingly close to the experimental values near 400 K. Then, one may anticipate that with increasing temperature beyond 420 K $^{139}\text{La} T_1^{-1}$ increases further and decreases ultimately, or gradually saturates, to a constant value that is close to $\sim 10 \text{ s}^{-1}$, being temperature-independent. This indicates that the ^{139}La relaxation rates at high temperatures near $J_{\text{ex}}/2$ are governed by the same local spin dynamics probed in the ^{63}Cu results.²⁶ Therefore, the $S = \frac{1}{2}$ antiferromagnetic 2D Heisenberg model^{29,30} may be indeed appropriate to describe the high temperature spin dynamics in LSCO even at $T \sim J_{\text{ex}}/2$.

Furthermore, we find that T_1^{-1} decreases linearly with temperature below 300 K down to ~ 150 K. This is clearly shown by T_1^{-1} divided by temperature, $(T_1 T)^{-1}$ (see the inset of Fig. 7). The Korringa-like behavior suggests that the relaxation process of the ^{139}La is dom-

inated by the doped hole carriers in this temperature range. Therefore, we ascribe the rapid drop of T_1^{-1} at high temperatures to an evolution from a paramagnetic regime at $T \geq J_{\text{ex}}/2$ to a regime below 300 K where the scattering with doped holes dominates the spin fluctuation properties, and thus the ^{139}La T_1^{-1} .

Below ~ 70 K, T_1^{-1} is enhanced in an extremely fast rate, which is ascribed to the critical slowing down of spin fluctuations associated with glassy spin freezing. Such a rapid upturn of T_1^{-1} is compatible with the significant broadening of the ^{139}La NMR spectrum in the same temperature range as shown in Fig. 5. Down to 4.2 K, a maximum of T_1^{-1} , which gives a characteristic spin freezing temperature T_g , was not identified. This is somewhat inconsistent with previous ^{139}La NMR results,^{17,18} and suggests a reduced T_g which is possibly related to less disorder in our sample.

IV. CONCLUSION

Through ^{139}La and ^{63}Cu NMR, we proved that the local tilting of the CuO_6 octahedra along $[110]_{\text{HTT}}$ occurs in the LTO phase, whereas it is absent in the HTT phase in $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$. The tilt direction of the CuO_6 octahedra alternates along the same direction resulting in the buckling of the CuO_2 plane. The structural order parameter representing the tilt angle of the CuO_6 octahedra was successfully obtained from the splitting of the ^{139}La resonance line as a function of temperature. The structural transition at $T_S = 387$ K is weakly first order and displacive i.e., the order parameter is reduced rapidly with increasing temperature approaching T_S , and abruptly vanishes in the HTT phase. In other words, the average HTT as well as the LTO phases are fully compatible with their local structures. Our data also rule out the possibility of an inhomogeneous mixture of the two phases in the whole temperature range measured in this study.

The ^{139}La spin-lattice relaxation rates, T_1^{-1} , exhibits a sharp anomaly at T_S , which is consistent with the abrupt change of the spectrum. The temperature dependence of T_1^{-1} in the high temperature region suggests that a temperature-independent paramagnetic regime at high temperatures changes gradually to a regime where the scattering with doped holes dominates the ^{139}La T_1^{-1} . The strong enhancement of T_1^{-1} below ~ 70 K is ascribed to the critical slowing down of spin fluctuations associated with glassy spin freezing.

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- ¹ B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, et al., Phys. Rev. B **46**, 14034 (1992).
 - ² J. D. Axe and M. K. Crawford, J. Low Temp. Phys. **95**, 271 (1994).
 - ³ B. Büchner, M. Breuer, A. Freimuth, and A. P. Kampf, Phys. Rev. Lett. **73**, 1841 (1994).
 - ⁴ A. Bianconi, N. L. Saini, A. Lanzara, M. Messori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito, Phys. Rev. Lett. **76**, 3412 (1996).
 - ⁵ B. J. Suh, P. C. Hammel, M. Hücker, and B. Büchner, Phys. Rev. B **59**, R3952 (1999).
 - ⁶ H.-H. Klauss, W. Wagener, M. Hillberg, W. Kopmann, H. Walf, F. J. Litterst, M. Hücker, and B. Büchner, Phys. Rev. Lett. **85**, 4590 (2000).
 - ⁷ J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature **375**, 561 (1995).
 - ⁸ H.-J. Grafe, N. J. Curro, M. Hücker, and B. Büchner, Phys. Rev. Lett. **96**, 017002 (2006).
 - ⁹ M. Vojta, Adv. Phys. **58**, 699 (2009).
 - ¹⁰ C. Friedrich, B. Büchner, M. M. Abd-Elmeguid, and H. Micklitz, Phys. Rev. B **54**, R800 (1996).
 - ¹¹ M. Braden, M. Meven, W. Reichardt, L. Pintschovius, M. T. Fernandez-Diaz, G. Heger, F. Nakamura, and T. Fujita, Phys. Rev. B **63**, 140510 (2001).
 - ¹² B. Simović, M. Hücker, P. C. Hammel, B. Büchner, U. Ammerahl, and A. Revcolevschi, Phys. Rev. B **67**, 224508 (2003).
 - ¹³ S. J. L. Billinge, G. H. Kwei, and H. Takagi, Phys. Rev. Lett. **72**, 2282 (1994).
 - ¹⁴ D. Haskel, E. A. Stern, D. G. Hinks, A. W. Mitchell, J. D. Jorgensen, and J. I. Budnick, Phys. Rev. Lett. **76**, 439 (1996).
 - ¹⁵ D. Haskel, E. A. Stern, F. Dogan, and A. R. Moodenbaugh, Phys. Rev. B **61**, 7055 (2000).
 - ¹⁶ S.-W. Han, E. A. Stern, D. Haskel, and A. R. Moodenbaugh, Phys. Rev. B **66**, 094101 (2002).
 - ¹⁷ M.-H. Julien, F. Borsa, P. Carretta, M. Horvatić, C. Berthier, and C. T. Lin, Phys. Rev. Lett. **83**, 604 (1999).
 - ¹⁸ M.-H. Julien, A. Campana, A. Rigamonti, P. Carretta, F. Borsa, P. Kuhns, A. P. Reyes, W. G. Moulton, M. Horvatić, C. Berthier, et al., Phys. Rev. B **63**, 144508 (2001).
 - ¹⁹ P. G. Radaelli, D. G. Hinks, A. W. Mitchell, B. A. Hunter, J. L. Wagner, B. Dabrowski, K. G. Vandervoort, H. K. Viswanathan, and J. D. Jorgensen, Phys. Rev. B **49**, 4163 (1994).
 - ²⁰ M. Lambacher, T. Helm, M. Kartsovnik, and A. Erb, Eur. Phys. J. Special Topics **188**, 61 (2010).
 - ²¹ G. C. Carter, L. H. Bennett, and D. J. Kahan, *Metallic shift in NMR* (Pergamon, New York, 1977).
 - ²² P. C. Hammel, A. P. Reyes, S.-W. Cheong, Z. Fisk, and J. E. Schirber, Phys. Rev. Lett. **71**, 440 (1993).
 - ²³ T. Nakano, M. Oda, C. Manabe, N. Momono, Y. Miura, and M. Ido, Phys. Rev. B **49**, 16000 (1994).
 - ²⁴ S. Wakimoto, H. Kimura, M. Fujita, K. Yamada, Y. Noda, G. Shirane, G. Gu, H. Kim, and R. J. Birgeneau, J. Phys. Soc. Jpn. **75**, 074714 (2006).
 - ²⁵ N. J. Curro, P. C. Hammel, B. J. Suh, M. Hücker, B. Büchner, U. Ammerahl, and A. Revcolevschi, Phys. Rev. Lett. **85**, 642 (2000).
 - ²⁶ T. Imai, C. P. Slichter, K. Yoshimura, and K. Kosuge, Phys. Rev. Lett. **70**, 1002 (1993).
 - ²⁷ S. Fujiyama, Y. Itoh, H. Yasuoka, and Y. Ueda, J. Phys. Soc. Jpn. **66**, 2864 (1997).
 - ²⁸ T. Moriya, Prog. Theor. Phys. **16**, 641 (1956).
 - ²⁹ S. Chakravarty and R. Orbach, Phys. Rev. Lett. **64**, 224 (1990).
 - ³⁰ M. P. Gelfand and R. R. P. Singh, Phys. Rev. B **47**, 14413 (1993).